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13. ABSTRACT (Maximum 200 words) Surfactant and lipid vesicles and their self-assembly processes are of interest in many fields including materials science. ^[1-13] The hollow spherical mesostructures find wide applications including drug delivery systems, cosmetics, pesticide carriers, models of biomembranes, catalysis, artificial photosynthesis, and microenvironment for template synthesis. ^[1-13] Approaches explored to address the fragility and instability of vesicles and liposomes include polymerizable surfactants and lipids, ^[4, 6, 11] cross-linking of the vesicles, ^[4] incorporation of polymerizable monomers into the vesicles, ^[4, 12] polymeric grafts onto the amphiphilic molecules, ^[5, 7] polymer coatings, ^[4, 5] and vesicle-templated polymerization. ^[13] Direct self-assembly of vesicles from polymeric amphiphiles represents an alternative strategy that could provide relatively more stable vesicles and mesostructures with novel properties and functions. In this paper we report the spontaneous self-assembly of highly stable spherical vesicles with outer diameters in the 200 nm to 200 µm range from new electroactive and photoactive, hydrogen-bonding, rod-coil-rod triblock copolymers. The conjugated polymer blocks in the vesicles are shown to form J-aggregates.				
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Spontaneous Self-Assembly of Vesicles From Electroactive and Photoactive Triblock Copolymers

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Surfactant and lipid vesicles and their self-assembly processes are of interest in many fields including materials science.^[1-13] The hollow spherical mesostructures find wide applications including drug delivery systems, cosmetics, pesticide carriers, models of biomembranes, catalysis, artificial photosynthesis, and microenvironment for template synthesis.^[1-13] Approaches explored to address the fragility and instability of vesicles and liposomes include polymerizable surfactants and lipids,^[4, 6, 11] cross-linking of the vesicles,^[4] incorporation of polymerizable monomers into the vesicles,^[4, 12] polymeric grafts onto the amphiphilic molecules,^[5, 7] polymer coatings,^[4, 5] and vesicle-templated polymerization.^[13] Direct self-assembly of vesicles from polymeric amphiphiles represents an alternative strategy that could provide relatively more stable vesicles and mesostructures with novel properties and functions. In this paper we report the spontaneous self-assembly of highly stable spherical vesicles with outer diameters in the 200 nm to 200 μ m range from new electroactive and photoactive, hydrogen-bonding, rod-coil-rod triblock copolymers. The conjugated polymer blocks in the vesicles are shown to form J-aggregates.

The size, shape, stability, durability, and physical properties of vesicles have been varied largely through the molecular structure of low molar mass amphiphiles and their self-assembly processes.^[1-13] Although polymerized or polymer-containing vesicles have also been widely used to tailor the structural and physical properties of vesicles,^[4, 6, 11-13] macromolecular amphiphiles have been scarcely explored except in a few theoretical suggestions of the possibility of spherical vesicle formation by diblock copolymers.^[14-16] Transmission electron

microscopy (TEM) observation of multiple aggregates (including vesicles) from a poly(styrene-*block*-acrylic acid) diblock copolymer solution has been reported.^[17] Recently, we observed the self-organization of a rod (A)-coil (B) *diblock* copolymer, A-NHCO-B, into several three-dimensional (3-D) assemblies including hollow spheres, tubules, lamellae, and doughnut-shaped mesostructures.^[18] Such a *polymorphism* is a familiar problem in crystal engineering^[19] and is a major challenge to the design and control of self-assembling synthetic mesostructures of desired *size*, *shape*, and *function*. We have now addressed the problem of polymorphism in macromolecular assemblies through chain architecture and find that spherical vesicles are uniquely self-assembled from new rod-coil-rod *triblock* copolymers.

Linear rod(A)-coil(B)-rod(A) triblock copolymers with a general structure A-NHCO-B-COHN-A were explored as a new class of macromolecular amphiphiles for the self-assembly of vesicles. Because the flexible-coil middle block B is tethered at both ends, each of the triblock copolymer chain is capable of adopting both a *linear* conformation and an intramolecularly *folded* or *looped* conformation. The two amide groups per chain make these block copolymers self-complementary building blocks that are capable of molecular recognition-driven self-organization^[20, 21] into hydrogen-bonded supramolecular assemblies (Fig. 1a). The curvature free energies that stabilize spherical vesicles^[14-16] can be expected to be very large in such monolayers or multilayers because of the rigid-rod blocks, triblock architecture, conformational asymmetry, and strong intermolecular hydrogen bonding. The new quinoline-styrene-quinoline (QSQ) triblock copolymers we synthesized (Fig. 1b) are structurally analogous to bolaamphiphiles^[4, 22] rather than conventional surfactants.^[1-13] The conjugated polyphenylquinoline (PPQ) blocks in QSQ open the prospects of preparing block copolymer vesicles with various electronic, optoelectronic, and photonic properties.^[23-25]

Three linear triblock copolymers, each with a fixed average sequence of the rodlike blocks ($N_A \sim 50$), were synthesized and characterized for our self-assembly studies: $N_B = 500$,

QSQ-1; $N_B = 250$, QSQ-2; and $N_B = 120$, QSQ-3. Solvent extractions, ^1H NMR and FTIR spectroscopies, and thermogravimetric analysis (TGA) were used to confirm the copolymer structures and compositions. Differential scanning calorimetry of the copolymers showed that they did not exhibit thermotropic mesophases. Both QSQ-1 and QSQ-2 copolymers had a T_g of 114°C , which is enhanced compared to PS homopolymer (100°C). QSQ-3 with PS block length of 120 did not exhibit a T_g in the range of -50 to 400°C .

Upon dissolving either QSQ-1 or QSQ-2 copolymer sample in a mixed solvent (trifluoroacetic acid: dichloromethane, TFA:DCM of various ratios) at room temperature (25°C), without sonication, mechanical stirring or other form of applied energy, spherical vesicles formed spontaneously from the dilute solutions (0.01 to 0.5 wt %). Polarized optical and fluorescence microscopies were used to visualize the triblock copolymer vesicles after drying solutions on a glass slide (Fig. 2). The diameter of the spheres was in the range of 1 to $200\ \mu\text{m}$ depending on the copolymer composition. The size distribution of vesicles of QSQ-1 was about 80% in the $20 - 40\ \mu\text{m}$ range (Fig. 2a, b), 10% in the $1 - 5\ \mu\text{m}$ range and 10% in the $50 - 200\ \mu\text{m}$ range; the typical QSQ-1 vesicle had a diameter of $\sim 27\ \mu\text{m}$. Vesicles of QSQ-2 were less polydisperse with $\sim 90\%$ with diameters in the $10 - 20\ \mu\text{m}$ range (Fig. 2c, d) and the remaining in the $1 - 5\ \mu\text{m}$ range. The average size of the QSQ-2 vesicles was $16\ \mu\text{m}$. Triblock copolymer QSQ-3 similarly spontaneously formed spherical, but highly perforated, vesicles with diameters of $1 - 5\ \mu\text{m}$ (80%) and $5 - 15\ \mu\text{m}$ ($\sim 20\%$) (Fig. 2e, f). The sizes of the randomly distributed holes in these perforated vesicles were polydisperse and as large as $0.5 - 1.0\ \mu\text{m}$. The results of our extensive investigation of the possible effects of solution drying temperature (20 to 95°C), concentration (0.01 to 0.5 wt %), and solvent ratio (TFA:DCM = 9/1 to 1/9) on the morphology of the vesicles, showed no effect of these variables on size and shape. However, vesicles were not observed by optical microscopy of any triblock copolymer solution at 0.001 wt % which

indicates either a critical concentration for vesiculation or vesicles with sizes below the resolution of optical microscopy.

It is remarkable that only *spherical vesicles* were formed from QSQ triblock copolymers under all self-assembly conditions tried. This contrasts sharply from the multiple morphologies observed in self-organized aggregates of a related *diblock* copolymer.^[18] This implies that spherical vesicles are the thermodynamically more stable aggregates of the *triblock* copolymers compared to planar lamellae, tubules, or other topologies. Another interesting feature of these block copolymer vesicles is their propensity for self-organization into higher order microstructures (Fig. 2). Highly ordered, close-packed hexagonal arrays of vesicles were commonly observed in QSQ-1 and QSQ-2 samples. Although some elastic deformation at the area of contact is commonly observed in soft colloidal particles or vesicles that aggregate,^[26] it is minimum in these block copolymer vesicles. It has been suggested that higher order assemblies of vesicles, such as observed here, could be used as simple models of biological tissue.^[26]

Visualization of the QSQ vesicles by scanning electron microscopy (SEM) confirmed the sizes and 3-D shape seen in optical microscopy and provided new information about the hollow cavity, wall thickness, and small diameter ($<1\ \mu\text{m}$) vesicles (Fig. 3). Dimples or partial flattening of the largest ($\sim 100\text{-}200\ \mu\text{m}$) vesicles were observed in only QSQ-1 (Fig. 3a). If the ca. 10-nm gold layer thickness is taken into account a wall thickness of about 360 nm is estimated from Fig. 3e, which means about 3 molecular layers of the 120-nm chains of QSQ-2. The wall thicknesses estimated from SEM for all the QSQ vesicles were in the range of 250 to 1,200 nm which indicates that they are multi-monolayered shells. The perforated vesicles seen only in QSQ-3 copolymer (Fig. 3c) are examples of the *sponge phase* which has previously been observed in several surfactant systems by freeze-fracture TEM and is currently of great theoretical and experimental interest for understanding self-avoiding multiconnected assemblies and phase transition phenomena.^[27, 28] About 5-10% of the QSQ-1 and QSQ-2 vesicles observed

in the SEM had diameters in the 200-800 nm range. Additional observations by TEM confirmed the size and relative amount of these smaller-diameter vesicles. These results suggest that the folded conformations of QSQ-1 and QSQ-2 are the building blocks for the self-assembly of the small-diameter (<800 nm) vesicles (Fig. 1).

Photoluminescence emission (PL) and excitation (PLE) spectra of the QSQ vesicles as solid films and as liquid dispersions showed that the conjugated polymer blocks formed J-aggregates within the vesicle shells (Fig. 4). The solid state PLE spectra of QSQ-1 and QSQ-2 vesicles both have a sharp peak at 423 nm and a shoulder at 463 nm, which are significantly red-shifted from the corresponding isolated chromophore with peak at 390 nm (Fig. 4a). QSQ-3 vesicles similarly have a red-shifted PLE spectrum with peaks at 423 and 477 nm. The PL spectra of all three types of QSQ vesicles have structureless emission bands centered at 598-608 nm, regardless of the excitation wavelength, which are significantly red shifted from the isolated QSQ chromophore which emits at 460 nm (Fig. 4a). The characteristic J-aggregate features^[29, 30] of the vesicles were more prominently observed in solution where the J-aggregation process was followed as a function of block copolymer concentration (Fig. 4b). In very dilute solution (10^{-5} wt %), where there is no aggregation, a broad absorption band centered at 388 nm with full width at half maximum (FWHM) of 77 nm was observed. At higher concentration (10^{-3} wt %) the absorption band seen in PLE is split into two Davydov components with peaks at 340 and 420 nm. At still higher concentration (10^{-2} wt %) where spherical vesicles are visible in optical microscopy, a more intense and sharp (FWHM = 21 nm) J-band absorption at 433 nm emerges. Only a small red shift of the emission band of the J-aggregates was observed compared to the isolated chromophore in solution. The relative fluorescence quantum yield of the solutions increased slightly with increasing concentration.

J-aggregation of the conjugated rodlike blocks of these vesicles implies that the chromophores are tilted at some angle whose variation can account for the observed spectral

variation with copolymer composition and also between solution and the solid state.^[29, 30] J-aggregation of dye molecules is well known to dramatically modify their photophysical properties while inducing novel *cooperative* optical properties such as high fluorescence quantum yield, exciton superradiance, and size dependent nonlinear optical properties.^[29, 30] The present results are the first evidence of J-aggregation of a macromolecular amphiphile or a copolymer containing π -conjugated polymer segments. Block copolymers containing conjugated blocks are thus a promising route to preparing well-defined, self-organized, J-aggregates which represent new forms of conjugated polymers that might exhibit novel phenomena and properties.

The self-assembled, highly luminescent and robust solid hollow spheres are ideal candidates for developing whispering gallery mode lasers where the dominant modes could be easily controlled by vesicle wall thickness and diameter.^[31] Concepts of optically or electrically triggered delivery systems are facilitated by electroactive and photoactive block copolymer vesicles. Synthetic macromolecular self-assembly and electroactive/photoactive supramolecular polymer assemblies are of fundamental interest in developing molecular devices of various types.^[21] In addition to the conventional applications of vesicles and liposomes, these electroactive and photoactive block copolymer vesicles may also find new uses in mesoscopic functional materials, polymer microsphere lasers, composites, photonic band gap structures, photovoltaic cells, and molecular optoelectronics. The results also exemplify strategies for the supramolecular self-assembly of hierarchical and functional mesostructures of well-defined size and shape from synthetic polymers.

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FIGURE CAPTIONS

- Figure 1.** **a**, Schematic of linear and folded conformations of the rod-coil-rod triblock copolymer in hydrogen-bonded supramolecular assemblies and resulting spherical vesicle. **b**, chemical structure of electroactive and photoactive QSQ triblock copolymer.
- Figure 2.** Polarized optical and fluorescence micrographs of solid vesicles dried from QSQ-1 (**a**, **b**), QSQ-2 (**c**, **d**), and QSQ-3 (**e**, **f**) triblock copolymer dispersions. Images in **a**, **c**, and **d**, were taken under cross-polarizers and the rest are fluorescence (540-nm excitation) images.
- Figure 3.** SEM images of vesicles from QSQ-1 (**a**), QSQ-2 (**b**, **d**, **e**, **f**) and QSQ-3 (**c**) copolymer solutions dried at 25°C. The broken vesicle in **d** is magnified in **e**.
- Figure 4.** **a**, PLE (monitored at 600 nm) and PL (excited at 460 nm) spectra of QSQ vesicles in the solid state as shown in Figure 2. Also, shown are the solid film PLE (monitored at 480 nm) and PL (390 -nm excitation) spectra of the isolated QSQ-2 copolymer dispersed in poly(ethylene oxide)(PEO) at 0.1 wt%. **b**, PLE and PL spectra of QSQ-2 solutions in 6:4 TFA:DCM at 25°C. PLE spectra (1,2,3) correspond to 540-nm emission and PL spectra (4,5) are for excitations from 330 to 430 nm.

Figure 1

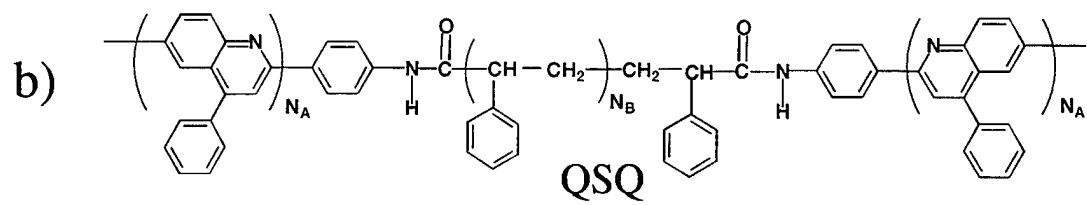
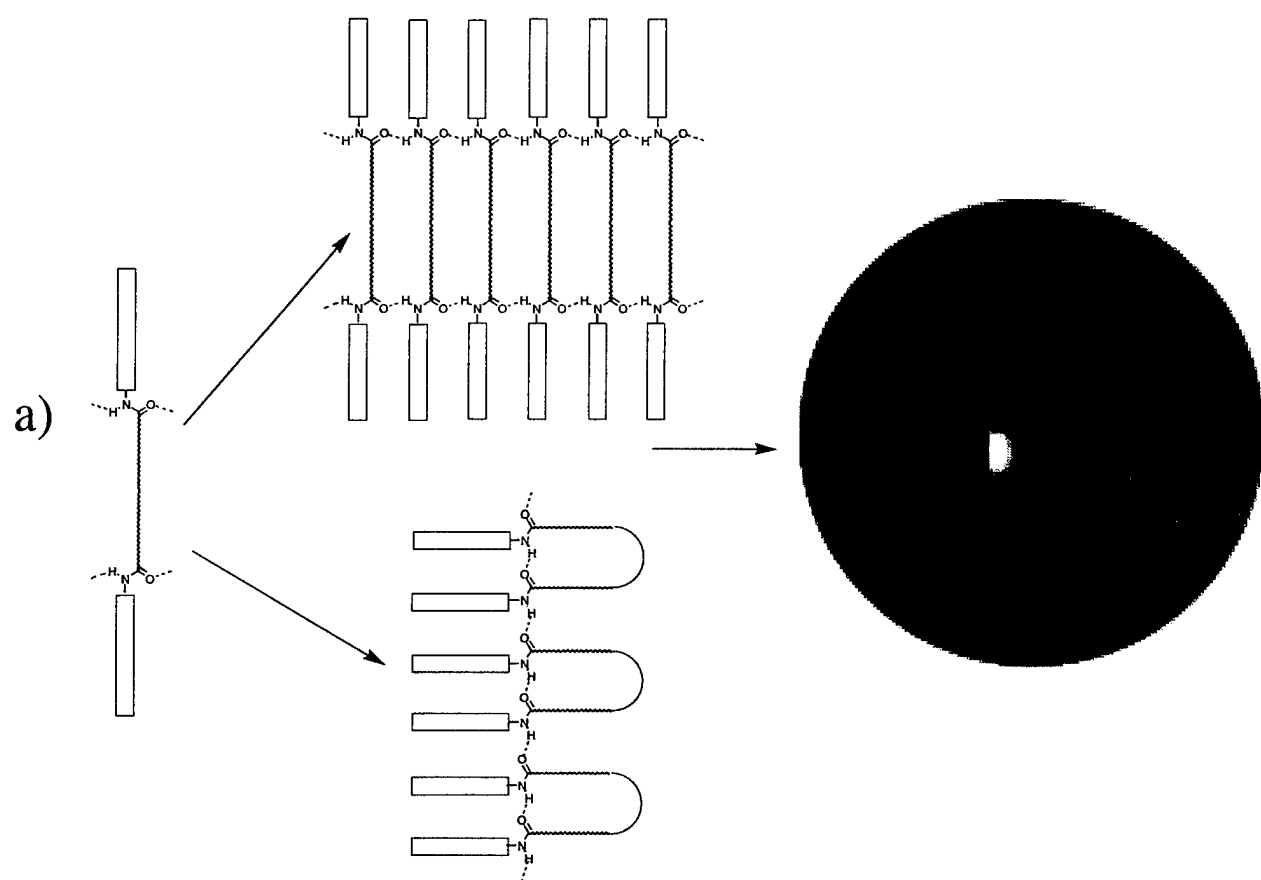


Figure 2

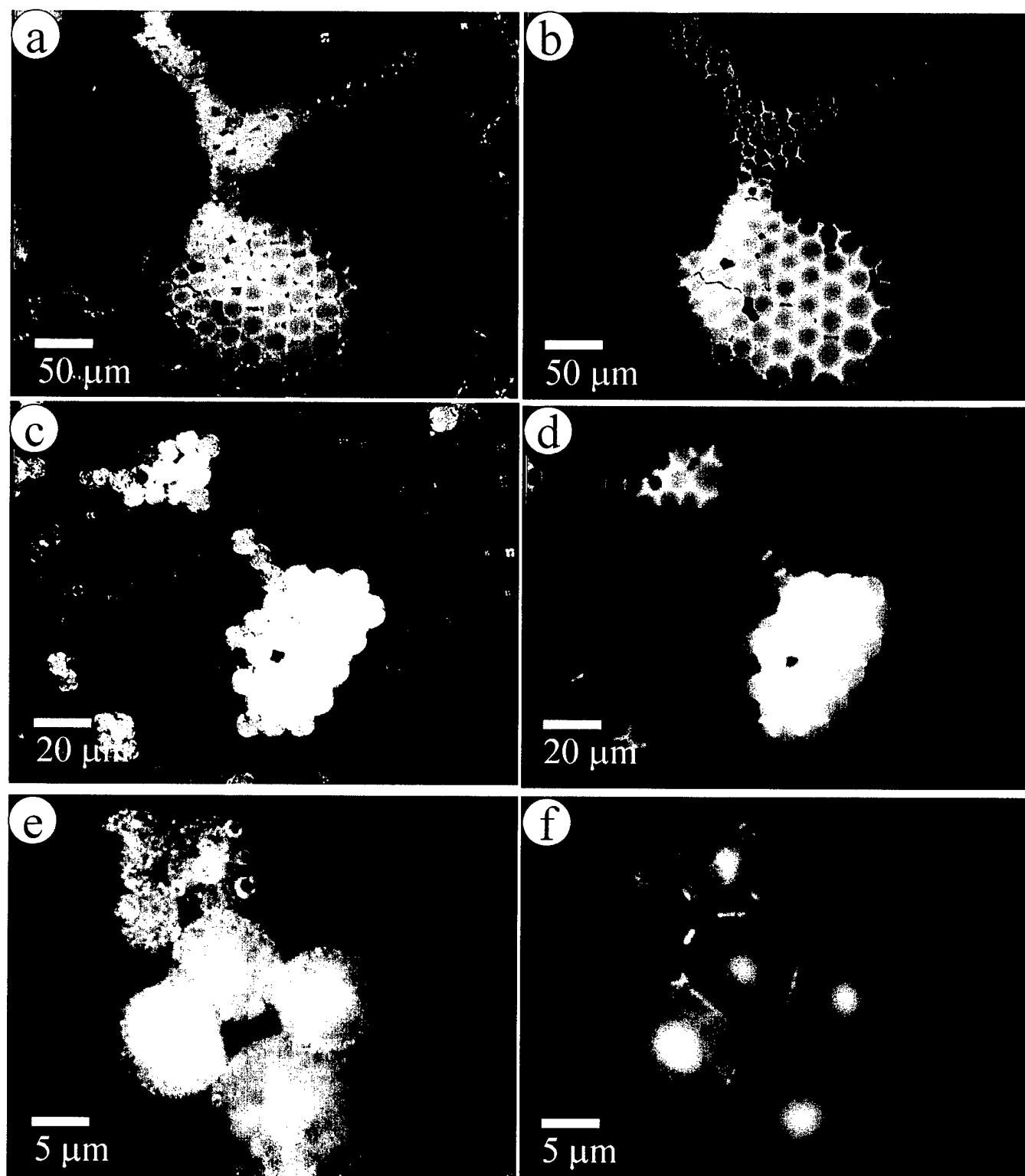


Figure 3

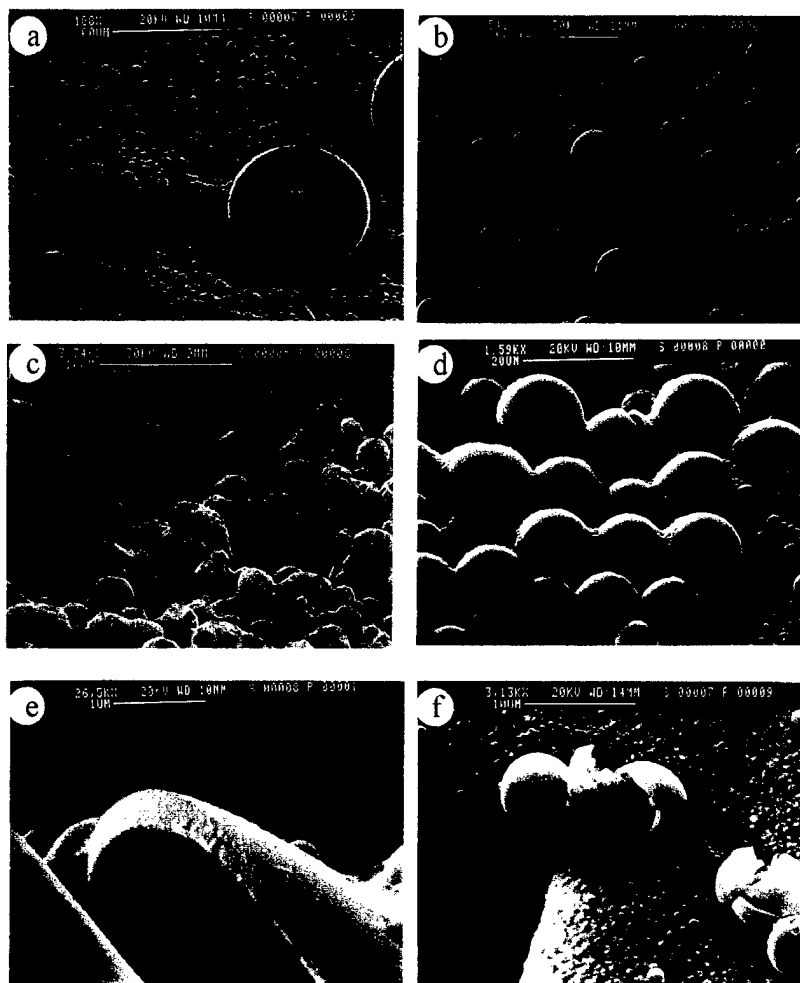


Figure 4

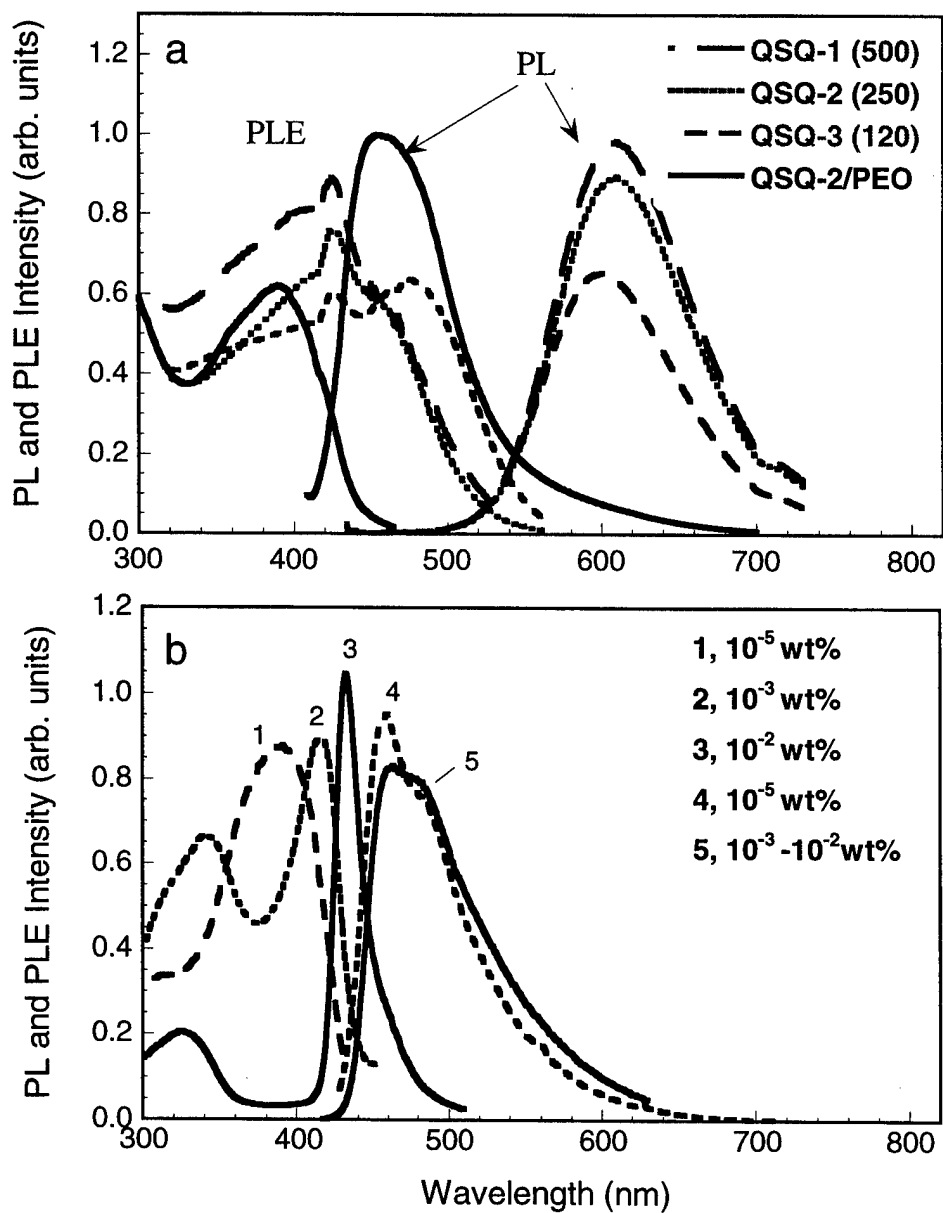


Figure 4

